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(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS FOR THE PREPARATION OF GLOBULAR  
SILICA PARTICLES

(70) van Beem, Martinus J.L.; Wagstaff, Nigel,  
Netherlands

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ABSTRACT

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It is known to prepare silica particles by the known sol-gel method. However silica particles prepared by the known method have a lower bulk crush strength and a lower water resistivity than desired. These properties of silica particles may be improved by the present invention which provides a process for the preparation of globular silica particles having a water resistivity of at least 80% and a bulk crushing strength of at least  $12 \text{ kg/cm}^2$ , which process comprises the following successive steps: a) preparing a silica hydrosol by mixing an aqueous solution of an alkali metal silicate with an aqueous solution of an acid, b) converting the hydrosol into droplet form, c) gelling the droplets in a liquid which is not miscible with water, d) removing at least 25% of the amount of water present in the hydrogel particles by evaporation, e) decreasing the alkali metal content of the hydrogel particles in an aqueous medium to less than 1% w calculated on dry material, and f) drying and calcining the globular silica particles. The so prepared silica particles are useful as catalysts, catalyst carriers, adsorbants, drying agents and ion exchangers.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the preparation of globular silica particles having a water resistivity of at least 80% and a bulk crushing strength of at least  $12 \text{ kg/cm}^2$ , which process comprises the following successive steps:
  - a) preparing a silica hydrosol by mixing an aqueous solution of an alkalimetal silicate with an aqueous solution of an acid,
  - b) converting the hydrosol into droplet form,
  - c) gelling the droplets in a liquid which is not miscible with water,
  - d) removing at least 25% of the amount of water present in the hydrogel particles by evaporation,
  - e) decreasing the alkalimetal content of the hydrogel particles in an aqueous medium to less than 1% w calculated on dry material, and
  - f) drying and calcining the globular silica particles.
2. A process as claimed in claim 1, in which at least 50% of the amount of water present in the hydrogel particles is removed by evaporation.
3. A process as claimed in claim 1 or 2, in which water is removed from the hydrogel particles by contacting them with a dry gas stream.
4. A process as claimed in claim 1 or 2, in which water is removed from the hydrogel particles by heating them.
5. A process as claimed in claim 1 or 2, in which water is removed from the hydrogel particles by contacting them with an inert liquid at a temperature above  $100^\circ\text{C}$ .
6. A process as claimed in claim 1 or 2, in which water is removed from the hydrogel particles by contacting them at an elevated temperature with steam or a steam-containing gas stream.

7. A process as claimed in claim 1 or 2, in which a quantity of filler, amounting to not more than 25% of the quantity of silica present in the hydrosol from which the silica particles are prepared, is incorporated into the silica particles.
8. Globular silica particles prepared according to a process as described in claim 1.
9. In a catalyst utilizing a particulate silica carrier the improvement comprising utilizing globular silica particles according to claim 8 as the carrier.
10. A process for the preparation of catalysts according to claim 9, in which the catalytically active metals are incorporated into the carrier prepared according to the process of claim 1 when the carrier is still in the hydro gel form.
11. A catalyst according to claim <sup>9</sup>~~10~~ wherein the catalytic element is a member of the group nickel, cobalt, molybdenum, tungsten, vanadium or a mixture thereof.
12. A catalyst according to claim <sup>9</sup>~~10~~ wherein the catalytic element is a member of the group molybdenum, tungsten, titanium, zirconium and vanadium.
13. In a process wherein a heavy oil or an olefinically unsaturated compound is contacted with a catalyst the improvement which comprises utilizing a catalyst according to claim <sup>9</sup>~~10~~.
14. A process according to claim 13 for the hydrodemetallization of a heavy hydrocarbon oil in which the heavy oil is contacted at elevated temperature and pressure and in the presence of hydrogen with a catalyst according to claim 11, which catalyst comprises at least one metal selected from the group consisting of nickel and cobalt and at least one metal selected from the group consisting of molybdenum, tungsten and vanadium as catalytically active metals.

15. A process according to claim 13 for the epoxydation of olefinically unsaturated compounds with an organic hydroperoxide in which the reactants are contacted with a catalyst according to claim 12, which catalyst comprises titanium as catalytically active metal.

SMART & BIGGAR  
OTTAWA, CANADA

PATENT AGENTS



The invention relates to a process for the preparation of globular silica particles having a high bulk crushing strength and water resistivity.

Silica particles are applied on a large scale,  
5 for example, as catalysts, catalyst carriers, adsorbents, drying agents and ion exchangers. For most of these applications globular particles of uniform shape with a high bulk crushing strength are preferred. An attractive way to prepare such particles is the well-known sol-gel  
10 method. According to this method a silica hydrosol is prepared by mixing an aqueous solution of an alkalimetal silicate with an aqueous solution of an acid. The hydrosol is converted into droplet form and the droplets are gelled in a liquid which is not miscible with  
15 water. After the alkalimetal content of the globular silica hydrogel particles has been reduced in an aqueous medium to less than 1 %w calculated on dry material, they are dried and calcined.

The expression "particles with a high bulk crushing  
20 strength" used in this patent application refers to particles having a bulk crushing strength of at least  $12 \text{ kg/cm}^2$ . According to the sol-gel method silica particles having such a high bulk crushing strength can easily be obtained. They show, however, a low water resistivity.  
25 This is a serious drawback if the silica particles are to be used for applications in which they have to be contacted with water, e.g. for the preparation



of silica-based catalysts by impregnation of the silica particles with an aqueous solution of compounds of catalytically active metals. Upon contacting the silica particles having a low water resistivity with water, 5 a considerable part of the particles shows cracks or disintegrates.

The expression "particles with a high water resistivity" used in this patent application refers to particles having a water resistivity of at least 80%. The water 10 resistivity of the globular silica particles is determined in a standard test in which 100 of the globular silica particles are contacted for 5 minutes at room temperature with a volume of water which amounts to 5times the volume of the 100 globular silica particles. Thereafter 15 the particles are inspected to determine the amount of particles which show cracks or have disintegrated. The water resistivity of the globular silica particles is expressed as the percentage of particles which have not been damaged by the contact with water.

20 It has now been found that globular silica particles having a high water resistivity can be prepared according to the sol-gel method, if at least 25% of the amount of water present in the silica hydrogel particles is removed therefrom by evaporation before their alkalimetal 25 content is decreased. It is very surprising that a water removal step at this point in the preparation procedure is capable of improving the water resistivity

of the ultimate silica particles, the more so as this water removal step is followed by a step which is carried out in an aqueous medium and as the preparation procedure comprises already as final step a water  
5 removal step. It has appeared that it is essential that the water removal step is carried out before the alkalimetal content of the particles is decreased and that the beneficial effect of this water removal step on the water resistivity of the ultimate silica  
10 particles is not affected adversely by the subsequent treatment of the particles in an aqueous medium.

The expression "water removal by evaporation" is used in this patent application to distinguish the present water-removal treatment from other treatments  
15 by which water is removed from silica hydrogels such as a treatment of the silica hydrogel particles with an aqueous solution of ammonia. It has been found that the latter treatment is capable of improving the water resistivity of the ultimate globular silica  
20 particles, but not to a degree sufficient to increase the water resistivity of the particles beyond the required 80% level. A serious drawback of this treatment, which makes it completely unsuitable for the present purpose is that as a result of this treatment the  
25 bulk crushing strength of the particles decreases dramatically to far below the required level of  $12 \text{ kg/cm}^2$ .



The invention therefore relates to a process for the preparation of globular silica particles having a water resistivity of at least 80% and a bulk crushing strength of at least  $12 \text{ kg/cm}^2$ , which process comprises the following successive steps: a) preparing a silica hydrosol by mixing an aqueous solution of an alkalimetal silicate with an aqueous solution of an acid, b) converting the hydrosol into droplet form, c) gelling the droplets in a liquid which is not miscible with water, d) removing at least 25% of the amount of water present in the hydrogel particles by evaporation, e) decreasing the alkalimetal content of the hydrogel particles in an aqueous medium to less than 1% w calculated on dry material, and f) drying and calcining the globular silica particles.

In addition to the possibility of preparing globular silica particles having a high water resistivity by the sol-gel method, the incorporation of the present water removal step has a cost saving effect, since smaller volumes of material have to be handled in the successive steps of the process.

In the process according to the invention, first of all a silica hydrosol is prepared by mixing an aqueous solution of an alkalimetal silicate with an aqueous solution of an acid. This may very suitably be performed by leading the starting solutions separately into a mixing chamber where mixing of the solutions takes

place by stirring. As alkalimetal silicate and as acid, sodium silicate and sulphuric acid, respectively, are very suitable. After the silica hydrosol has been formed it is converted into droplet form and gelled in a liquid which is not miscible with water. This may very suitably be performed by introducing the hydrosol via a small aperture in the bottom of the mixing chamber into the upper end of a vertically disposed tube filled with oil. Gelation occurs while the hydrosol droplets move downwards through the oil. At the bottom of the tube the globular hydrogel particles may be caught in water, separated from the water e.g. by filtration, washed with water and thereafter subjected to the water removal step. It is also possible to carry out the water removal step in the same oil wherein gelation has taken place.

In the water removal step according to the invention at least 25% and preferably at least 50% of the water present in the hydrogel particles is removed therefrom by evaporation. This water removal step may be carried out in various ways. Water may e.g. be removed from the hydrogel particles by contacting them with a dry gas stream, e.g. a stream of dry air either or not at elevated temperature. Water may also be removed from the hydrogel particles by heating them at atmospheric pressure or at reduced or elevated pressure. Other ways of removing water from the hydrogel particles are contacting them with an inert liquid at a temperature above 100°C

or contacting them at elevated temperature with steam or a steam-containing gas stream. Examples of treatments which may very suitably be applied for removing at least 25% of the water present in the hydrogel particles are

5 the following:

- a) heating the hydrogel particles at a temperature of about 100°C at reduced pressure,
- b) heating the hydrogel particles at a temperature above 100°C in a stream of air,
- 10 c) heating the hydrogel particles at a temperature of about 100°C at reduced pressure followed by heating the particles at a temperature of about 500°C in a stream of air,
- d) contacting the hydrogel particles with a hydrocarbon oil at a temperature above 100°C,
- 15 e) heating the hydrogel particles at a temperature above 100°C in an autoclave at autogeneous pressure, and
- f) heating the hydrogel particles in a stream of air and steam.
- 20

After the treating step in which at least 25% of the water present in the hydrogel particles is removed therefrom by evaporation, the alkalimetal content of the hydrogel particles is decreased in an aqueous medium to less than 1 %w calculated on dry material. This alkalimetal removal may very suitably be performed by treating the hydrogel particles with an aqueous solution of ammonium

25

nitrate until the desired low alkalimetal content has been reached.

Finally the hydrogel particles are dried and calcined. Drying and calcining of the hydrogel particles may e.g. be carried out by heating the particles for a certain period of time at a temperature of 100-200°C and 450-550°C, respectively.

If desired, a small amount of a filler may be incorporated into the silica particles according to the invention.

10 Incorporation of a filler may be attractive for various reasons. In the first place the porosity of the ultimate silica particles may be influenced by this measure. Further, for certain applications of the silica particles, the presence of e.g. an alumina filler therein may be  
15 attractive. It is also possible to decrease the cost of preparation of the silica particles by incorporating therein a cheap filler. The incorporation of the filler into the silica particles may very suitably be performed by adding the filler to the aqueous solution of the  
20 alkalimetal silicate and/or to the aqueous solution of the acid from which the hydrosol is prepared by mixing. Examples of suitable fillers are kaolin, montmorillonite, bentonite, precipitated silica fillers, aluminas, zeolites and amorphous precipitated silica-aluminas.

25 With respect to the amount of filler which may be incorporated into the silica particles according to the invention, it has been found that the presence

of a filler in the ultimate silica particles reduces the bulk crushing strength of the particles, which effect is more pronounced according as the filler content of the particles is higher. Since, however, the sol-gel method as a rule provides globular silica particles with a very high bulk crushing strength, a small decrease is of no importance, and filler containing globular silica particles which amply comply with the requirement that the bulk crushing strength should amount to at least 12 kg/cm<sup>2</sup> can be easily prepared, provided that the quantity of filler incorporated therein amounts to not more than 25% of the quantity of silica present in the hydrosol from which the silica particles are prepared. Incorporation of larger amounts of filler in the silica particles entails the risk that silica particles with a bulk crushing strength below 12 kg/cm<sup>2</sup> are obtained, and therefore falls outside the scope of the present patent application.

Globular silica particles prepared according to the present invention may be applied e.g. as catalysts, catalyst carriers, adsorbents, drying agents and ion exchangers. They are of particular importance as carriers for one or more metals with catalytic activity. Catalysts comprising the present silica particles as carrier may be applied in various processes in the chemical and petroleum industries. The preparation of the catalysts may be carried out by any technique for the preparation

of supported catalysts known in the art, e.g. by impregnating the globular silica particles with an aqueous solution comprising salts of the catalytically active metals concerned, followed by drying and calcining of the composition.

5 An attractive way of preparing the present catalysts is one in which the catalytically active metals are incorporated into the carrier in an early stage of the carrier preparation, e.g. when the latter is still in the hydrogel form. Not only can the porosity of the  
10 ultimate catalyst be influenced, but also this method of preparation offers the advantage that the additional drying and calcining steps required after impregnation become superfluous.

Globular silica particles prepared according to  
15 the invention are of particular importance as carriers for catalysts which are used in the hydrodemetallization of heavy hydrocarbon oils and in the epoxidation of olefinically unsaturated compounds with an organic hydroperoxide.

Hydrodemetallization of heavy hydrocarbon oils  
20 is a well-known process in the petroleum industry and is applied, amongst other things, to decrease the metal content of heavy hydrocarbon oils which are to be used as feed for catalytic treating processes such as hydrodesulphurization or catalytic conversion processes such as hydro-  
25 cracking and catalytic cracking. As a result of the demetallization, the life of the catalyst in the subsequent treating or conversion process is prolonged. Hydrodemetallization is carried out by contacting the heavy hydrocarbon oil

of molybdenum, tungsten, titanium, zirconium and vanadium on a silica carrier. Especially preferred are catalysts comprising titanium on a silica carrier. Globular silica particles prepared according to the present invention are preferred carriers for these catalysts.

The invention will now further be elucidated with the aid of the following examples.

Comparative Example A

An aqueous sodium waterglass solution comprising 12 %w  $\text{SiO}_2$  and having a  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio of 0.3 was mixed continuously in a mixing chamber with an aqueous 1.2 N sulphuric acid solution in a volume ratio acid solution/waterglass solution of 0.75. After a residence of a few seconds in the mixing chamber the hydrosol obtained was converted into droplet form and the hydrosol droplets allowed to fall through a vertically disposed cylindrical tube with a length of 1.8 m filled with a paraffinic hydrocarbon oil of 25°C. During the fall through the tube gelation occurred. The globular hydrogel particles were caught at the bottom of the tube in water of 25°C. After the globular hydrogel particles had been separated by filtration they were washed with water. The water content of these globular hydrogel particles was determined in a standard test in which a sample was heated in three hours from room temperature to 600°C and thereafter kept at 600°C for one hour. The water content of the hydrogel particles appeared to be 90 %w.

at elevated temperature and pressure in the presence of hydrogen with a catalyst. Preferred catalysts for this purpose are catalysts comprising one or more metals selected from the group consisting of nickel, cobalt,

5 molybdenum, tungsten and vanadium on a silica carrier.

Especially preferred are catalysts comprising at least one metal selected from the group consisting of nickel and cobalt and at least one metal selected from the group consisting of molybdenum, tungsten and vanadium,

10 such as the metal combination nickel/vanadium, nickel/molybdenum and cobalt/molybdenum on a silica carrier. Globular silica particles prepared according to the present invention are preferred carriers for these catalysts.

Epoxidation of olefinically unsaturated compounds  
15 with an organic hydroperoxide is a well-known process in the chemical industry and is applied, amongst other things, for the preparation of propylene oxide and epichlorohydrin from propylene and allyl chloride, respectively. The epoxidation of olefinically unsaturated compounds with  
20 an organic hydroperoxide is carried out by contacting the reactants preferably at elevated temperature and pressure with a catalyst. As organic hydroperoxide ethyl benzene hydroperoxide is preferred, since the methylphenylcarbinol which is obtained as a by-product in the reaction may  
25 easily be converted into the valuable styrene. Preferred catalysts for the epoxidation are catalysts comprising at least one metal selected from the group consisting



Water contents of silica hydrogel particles mentioned in the following examples have all been determined by the above-described standard test.

Comparative Example B

5           A portion of the silica hydrogel particles with a water content of 90 %w prepared according to example A was treated with an aqueous 0.1 M ammonium nitrate solution at room temperature until the sodium content of the particles had been decreased to 0.2 %w calculated  
10           on dry material. After drying for 2 hours at 100°C and calcining for 3 hours at 500°C the globular silica particles thus obtained showed a water resistivity of 30% and a bulk crushing strength above 16.7 kg/cm<sup>2</sup>. (16.7 kg/cm<sup>2</sup> is the maximum value which can be measured with the  
15           bulk crushing strength determination method applied.)

EXAMPLE I

          A portion of the silica hydrogel particles with a water content of 90 %w prepared according to example A was dried for 2 hours at 100°C at reduced pressure.  
20           After this treatment the water content of the hydrogel particles amounted to 18 %w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in example B. The globular silica particles  
25           thus obtained showed a water resistivity of 95% and a bulk crushing strength above 16.7 kg/cm<sup>2</sup>.

EXAMPLE II

A portion of the silica hydrogel particles with a water content of 90 %w prepared according to example A was dried for 3 hours at 120°C in a stream of air.

5 After this treatment the water content of the hydrogel particles amounted to 14 %w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in example B. The globular silica particles  
10 thus obtained showed a water resistivity of 93% and a bulk crushing strength above 16.7 kg/cm<sup>2</sup>.

EXAMPLE III

A portion of the silica hydrogel particles with a water content of 90 %w prepared according to example  
15 A was dried for 2 hours at 100°C at reduced pressure and thereafter calcined for 3 hours at 500°C in a stream of air. After this treatment the water content of the particles amounted to 3 %w. Subsequently the particles were treated with an aqueous solution of ammonium nitrate,  
20 dried and calcined in the same way as the hydrogel particles in example B. The globular silica particles thus obtained showed a water resistivity of 95% and a bulk crushing strength above 16.7 kg/cm<sup>2</sup>.

EXAMPLE IV

25 A portion of the silica particles with a water content of 90 %w prepared according to example A was kept in contact with a paraffinic hydrocarbon oil at

150°C for 6 hours. After this treatment the water content of the particles had decreased to 12 %w. Subsequently the particles were treated with an aqueous solution of ammonium nitrate dried and calcined in the same way.

5 as the hydrogel particles in example B. The globular silica particles thus obtained showed a water resistivity of 96% and a bulk crushing strength above 16.7 kg/cm<sup>2</sup>.

#### EXAMPLE V

10 A portion of the silica particles with a water content of 90 %w prepared according to example A was heated for 1½ hour at 185°C at autogeneous pressure in an autoclave. After this treatment the water content of the hydrogel particles amounted to 15 %w. Subsequently the hydrogel particles were treated with an aqueous  
15 solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in example B. The globular silica particles thus obtained showed a water resistivity of 94 % and a bulk crushing strength above 16.7 kg/cm<sup>2</sup>.

#### 20 EXAMPLE VI

This example was carried out substantially in the same way as example I, however, in the present case the aqueous sodium waterglass solution contained 12 g powdered kaolin filler per litre (this corresponds to  
25 10% of the quantity of silica present in the sol). The ultimate globular silica particles showed a water resistivity of 91 % and a bulk crushing strength of 15 kg/cm<sup>2</sup>.

EXAMPLE VII

A portion of the silica particles with a water content of 90 %w prepared according to Example A was heated for 4 hours at 120°C at autogeneous pressure in an autoclave. After this treatment the water content of the hydrogel particles amounted to 60 %w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in Example B.

5 The globular silica particles thus obtained showed a water resistivity of 98 % and a bulk crushing strength above 16.7 kg/cm<sup>2</sup>.

Comparative example C

This example was carried out in substantially the same way as example I, however, in the present case the aqueous sodium waterglass solution contained 72 g powdered kaolin filler per litre (this corresponds to 60% of the quantity of silica present in the sol). The ultimate globular silica particles showed a water resistivity of 85 % and a bulk crushing strength of 10 kg/cm<sup>2</sup>.

Comparative example D

A portion of the silica hydrogel particles with a water content of 90 %w prepared according to example A was covered for 16 hours at room temperature with an aqueous solution containing 25 %w ammonia. After this treatment the water content of the hydrogel particles amounted to 30 %w. Subsequently the hydrogel particles

were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in example B. The globular silica particles thus obtained showed a water resistivity of 45% and a bulk crushing strength of 5 kg/cm<sup>2</sup>.

Comparative example E

A portion of the silica particles with a water content of 90 %w prepared according to example A was heated for  $\frac{1}{2}$  hour at 120°C at autogeneous pressure in an autoclave. After this treatment the water content of the hydrogel particles amounted to 72 %w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in example B. The globular silica particles thus obtained showed a water resistivity of 50 % and a bulk crushing strength of 8 kg/cm<sup>2</sup>.